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**Source to sink: Evolution of lignin composition in the Madre de Dios River system with connection to the Amazon basin and offshore**

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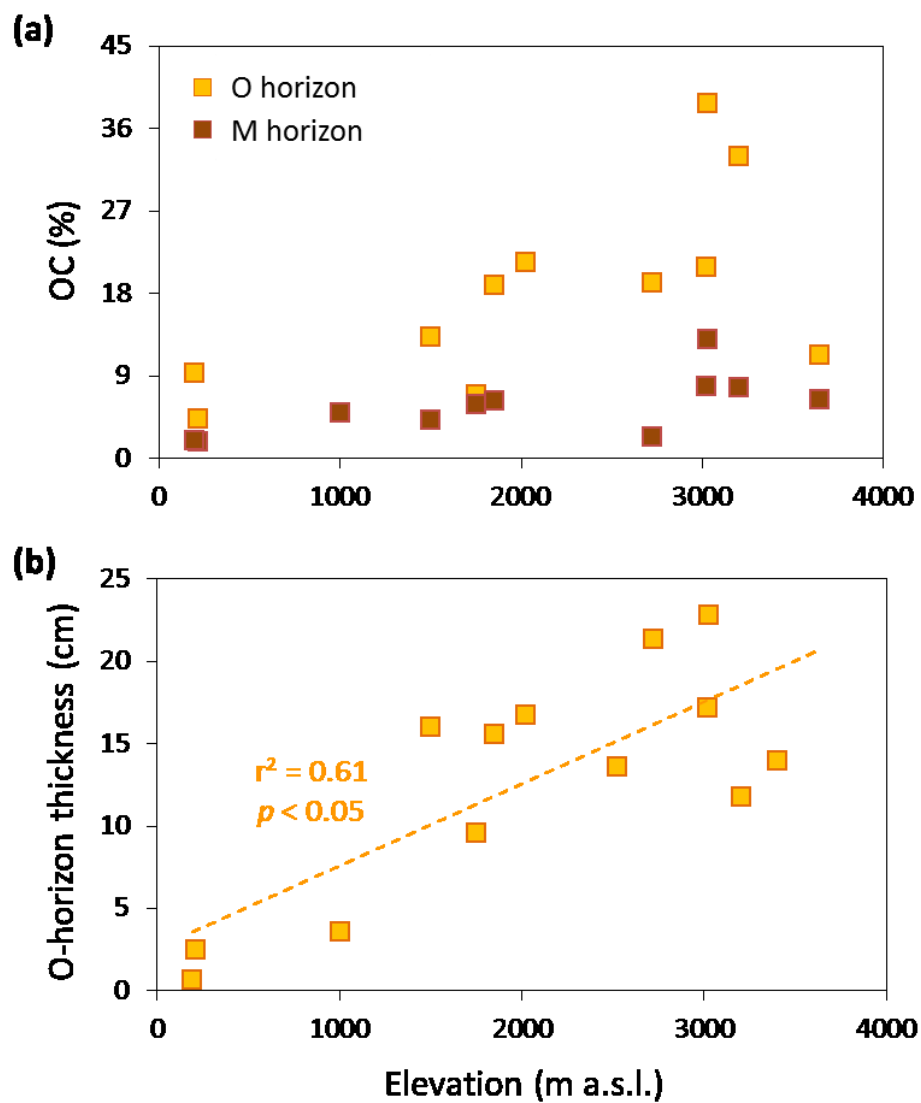
Captions for Tables S1

**Introduction**

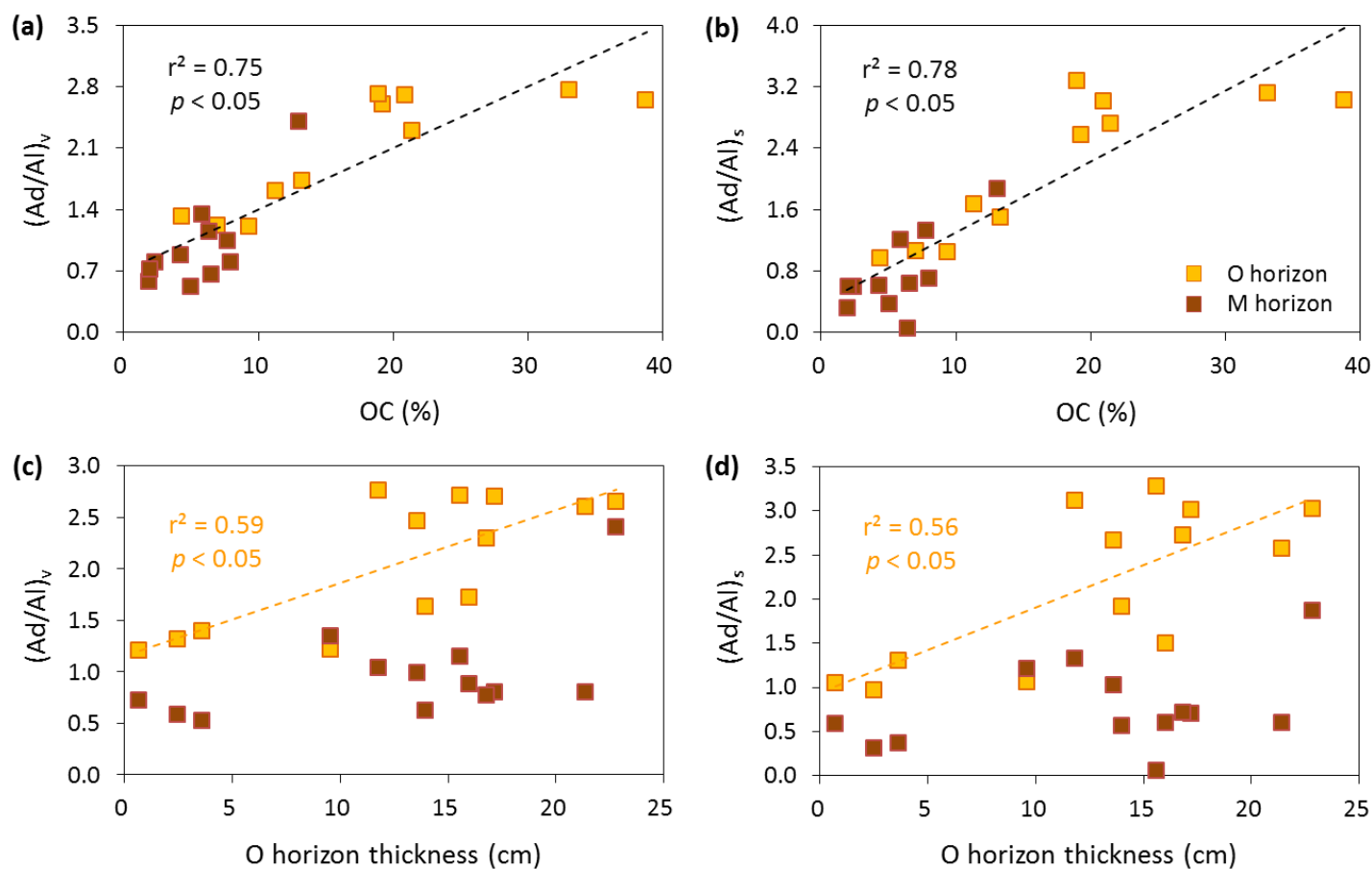
This supporting information provides supplementary discussion on the environmental controls on lignin distribution in soils (Text S1), figures of soil organic carbon content and O-horizon thickness along the elevation gradient (Figure S1), soil acid-to-aldehyde ratio changes with soil organic carbon (OC) content and O-horizon thickness (Figure S2), changes of lignin parameters in the surface POM (Figure S3), comparison of phenol composition in the particulate organic matter (POM) and dissolved organic matter (DOM) of Madre de Dios River (Figure S4), correlations of specific surface area (SSA) with POM components (Figure S5), and relationships of lignin phenol concentrations with net primary productivity and mean annual temperature in the Peruvian Andes-Amazon forests (Figure S6).

### **Text S1. Environmental controls on lignin distribution in soils**

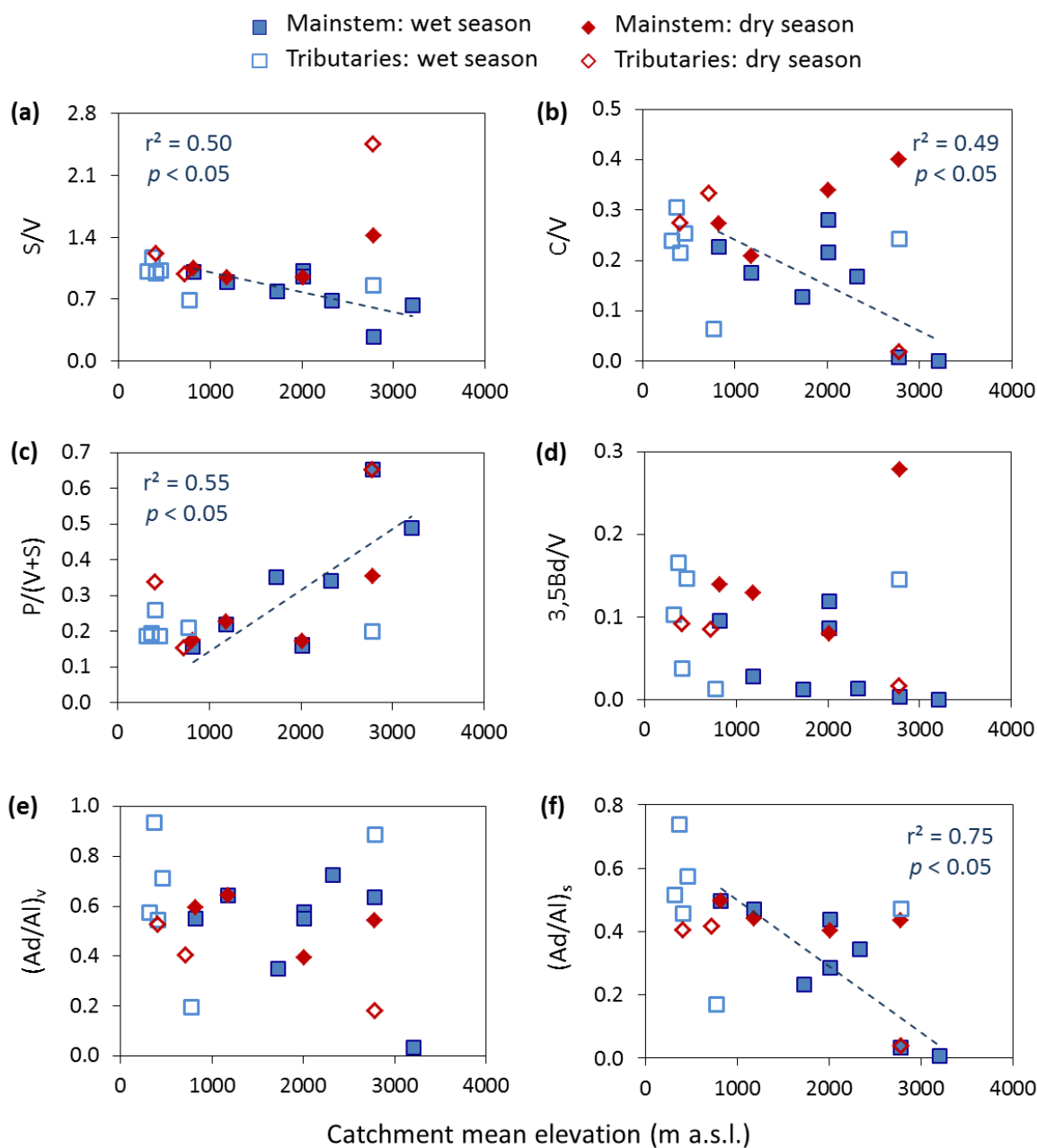
Across the study region, with increasing forest net primary productivity (NPP),  $\Lambda_{\text{lignin}}$  increased in the O horizon ( $p < 0.05$ ; Supplementary Figures S6a-b) but not in the mineral soils. As lignin is among the most hard-to-decay components in forest litter [Derenne and Largeau, 2001; Gleixner et al., 2001], shifts in its abundance in the O horizon are dominated by inputs (i.e., NPP). In the mineral soils, however, lignin is not observed to accumulate [Grandy and Neff, 2008; Marschner et al., 2008] and decomposition processes are more important than inputs in regulating lignin abundances. Therefore, elevated lignin inputs resulting from increased NPP at lower elevations and at higher MATs [Girardin et al., 2014; Huaraca Huasco et al., 2014; Malhi et al., 2014] likely contribute to the negative correlation of  $\Lambda_{\text{lignin}}$  with elevation in the O horizons ( $r^2 = 0.58$ ,  $p < 0.05$ ; Figure 2a) and the positive correlation of  $\Lambda_{\text{lignin}}$  with MAT in both horizons ( $p < 0.05$ ; Figure S6c) but showing a much smaller slope in the mineral horizons in the latter regression. Other biomarkers (including P phenols, 3,5Bd and cutin acids) and soil OC did not show any correlation with NPP or MAT. MAP did not exert any effect on soil biomarker concentrations (including  $\Lambda_{\text{lignin}}$ ) or soil OC content in the study area.



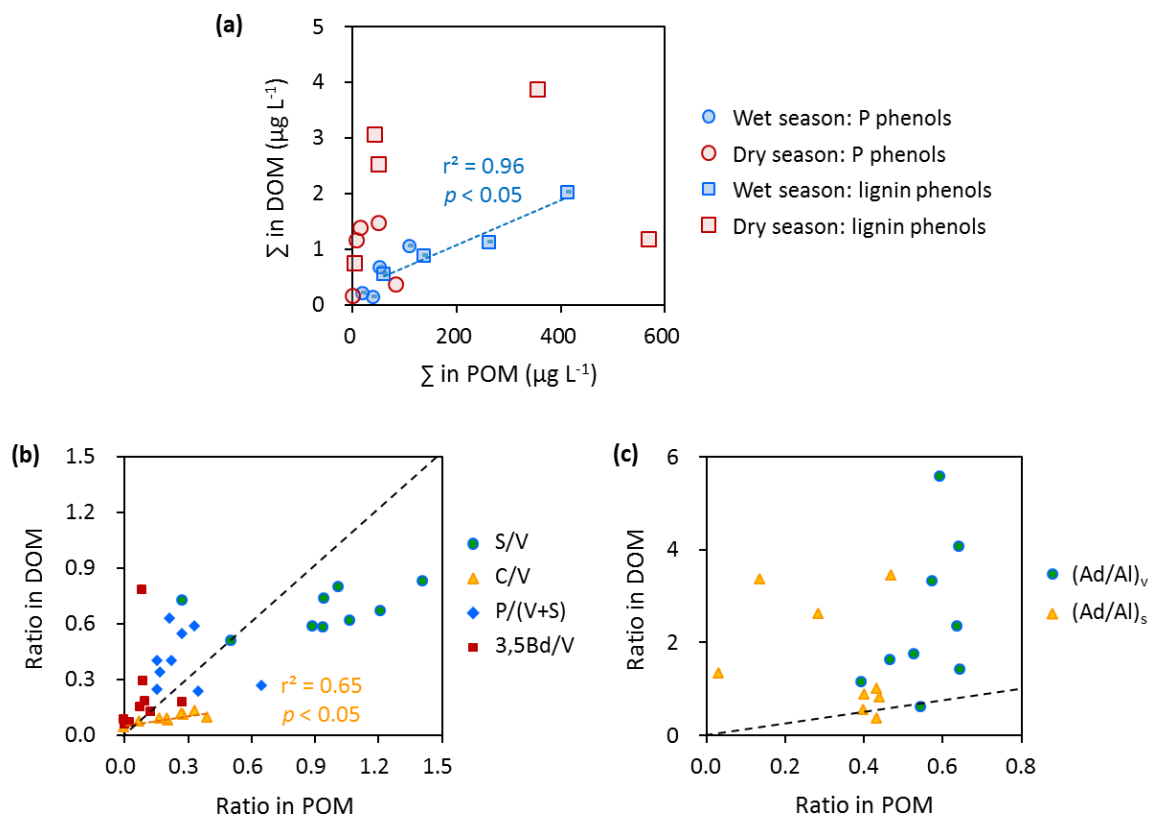
**Figure S1.** Change of soil organic carbon (OC) content in the organic (O) and surface mineral (M) horizons (a) and O-horizon thickness (b) of Peruvian Andes-Amazon forests with elevation. Dotted line represents linear regression ( $p < 0.05$ ); a.s.l.: above sea level.



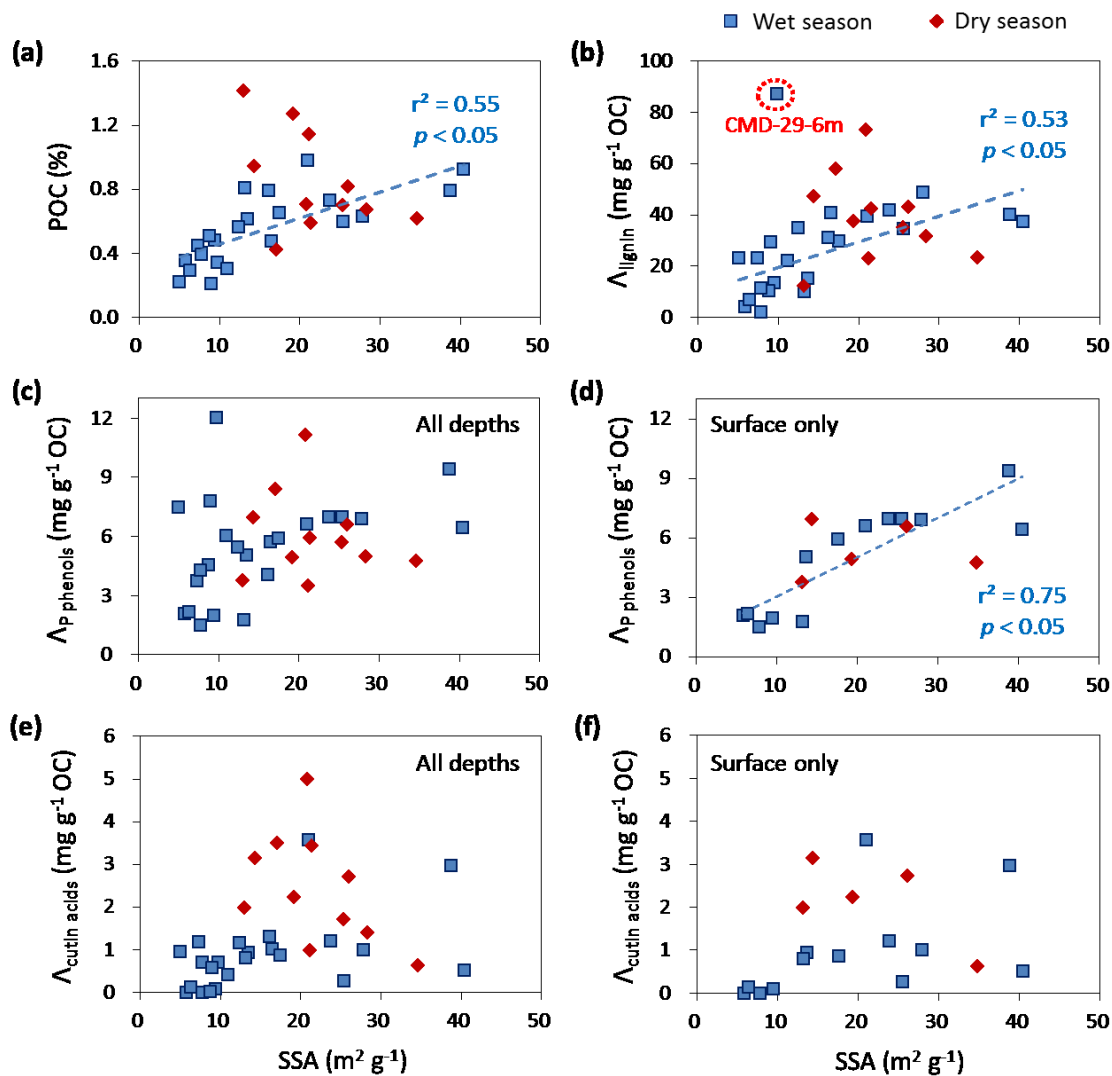
**Figure S2.** Comparisons of the acid-to-aldehyde ratios (Ad/Al) of vanillyl and syringyl phenols with soil organic carbon (OC) content in the organic (O) and surface mineral (M) horizons (a and b) and O horizon thickness (c and d) of Peruvian Andes-Amazon forests. Black and orange dotted lines represent linear regressions of both horizons and O horizons only, respectively ( $p < 0.05$ ).



**Figure S3.** Changes of lignin parameters in the surface particulate organic matter of Kosñipata and Madre de Dios Rivers with elevation: ratios of S/V (a), C/V (b), P/V+S (c), 3,5Bd/V (d), (Ad/Al)<sub>v</sub> (e), and (Ad/Al)<sub>s</sub> (f). Abbreviations as in Figure 3. Blue dotted lines represent linear regressions of mainstem samples in the wet season ( $p < 0.05$ ).

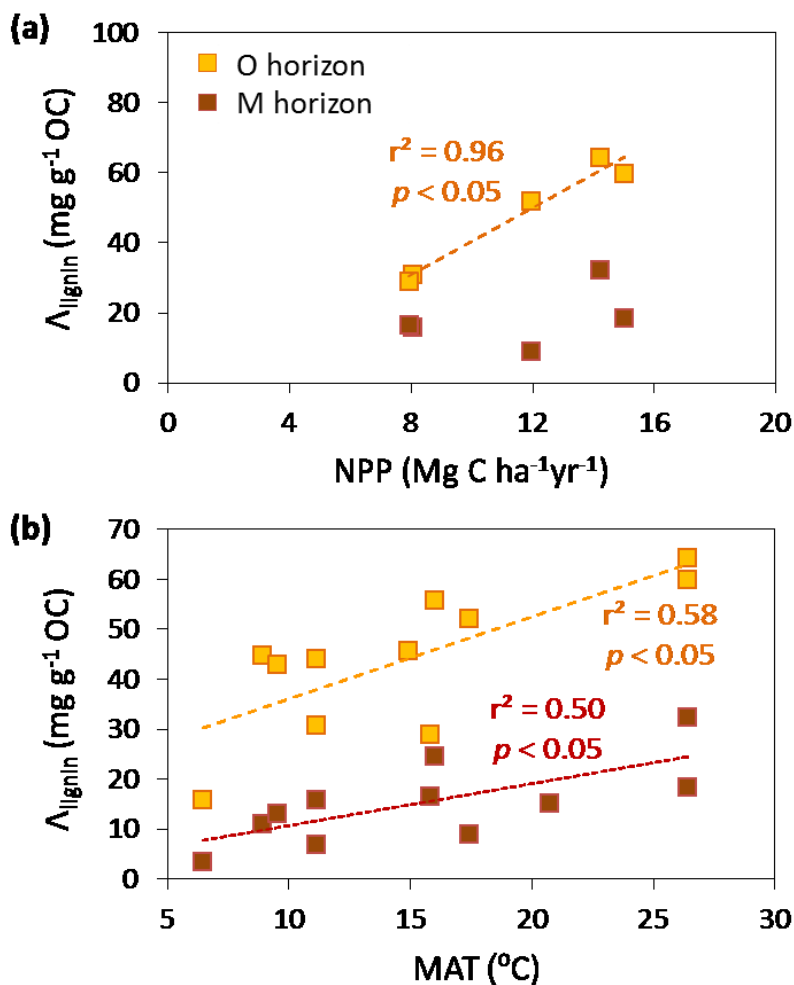


**Figure S4.** Comparison of lignin and *p*-hydroxyl (P) phenol concentrations (a) and compositions (b and c) in the particulate organic matter (POM) and dissolved organic matter (DOM) in the Madre de Dios River. Refer to the caption of Figure 3 for the abbreviation of parameters. Black dashed line represents 1:1 line in b and c. Colored dotted lines represent linear regressions of the corresponding symbols where significant ( $p < 0.05$ ).



**Figure S5.** Correlations of specific surface area (SSA) with particulate organic carbon (POC) content (a) and organic carbon (OC)-normalized concentration ( $\Lambda$ ) of lignin (b), *p*-hydroxyl (P) phenols (c and d) and cutin acids (e and f) in the particulate organic matter of Madre de Dios River at all depths (a-c, e) and in surface waters (d and f). Blue dotted lines represent linear regressions of wet-season samples ( $p < 0.05$ ). Data point in red dotted circle in b is excluded as an outlier.





**Figure S6.** Relationships of organic carbon (OC)-normalized concentration ( $\Lambda$ ) of lignin phenols in the organic (O) and surface mineral (M) horizons of Peruvian Andes-Amazon forests with net primary productivity (NPP; a) and mean annual temperature (MAT; b). NPP data are obtained from *Girardin et al.* [2014], *Huaraca Huasco et al.* [2014], *Malhi et al.* [2014]. Orange and red dotted lines represent linear correlations in O and M horizons, respectively ( $p < 0.05$ ).

**Table S1.** Location and biomarker composition in soils, riverine suspended particulate matter (SPM), dissolved organic matter (DOM) and marine surface sediments of the Madre de Dios-Amazon system.